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## (54) PRODUCTION OF ANHYDROUS CHROMIC CHLORIDE

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, British corporation established by Statute, of Kingsgate House, 66-74 Victoria Street, London S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following

This invention is concerned with the production of anhydrous chromic chloride.

Anhydrous chromic chloride,  $\text{CrCl}_3$ , is a substantially water insoluble, violet compound which is readily reduced with hydrogen to form chromous chloride,  $\text{CrCl}_2$ , and chromium sponge, this reduction being the basis of a chromising process.

It is known to produce chromic chloride by the chlorination of chromic oxide with chlorine oxide with chlorine in the presence of carbon or with carbon tetrachloride at temperatures substantially in excess of  $600^\circ\text{C}$ . Because of the highly corrosive nature of the reactants at such temperatures, the reaction must be carried out in equipment made of suitably corrosion-resistant material, such as graphite, fused silica, or high purity alumina; conventional metallic equipment made, for example, of stainless steel, cannot be used. In addition, the product has to be purified by sublimation, if desired in a stream of dry chlorine gas, and condenses as a voluminous mass of micaceous crystals that are difficult to handle.

We have now developed an improved process for the preparation of anhydrous chromic chloride which can be carried out at temperatures below  $600^\circ\text{C}$ , which can be carried out in reaction equipment formed of certain metals, which does not require sublimation of the product to purify it, and which gives a product having a bulk density such that the product can

be easily handled.

According to the present invention, there is provided a process for the preparation of anhydrous chromic chloride, which comprises chloridising chromic oxide hydrate,  $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , with a vapour or gas phase chloridising agent at an elevated temperature which is below the glow temperature (at which anhydrous chromic oxide recrystallises) and then cooling the anhydrous chromic chloride obtained in a non-oxidising atmosphere.

Suitable chloridising agents are, for example, carbon tetrachloride vapour; other gaseous or vaporised chlorohydrocarbons; mixtures of carbon monoxide and chlorine; phosphine; and mixtures of carbon monoxide and vaporised chlorohydrocarbons, of which the first, carbon tetrachloride vapour, is preferred. The chloridising agent is preferably used in admixture with an inert gas, such as nitrogen.

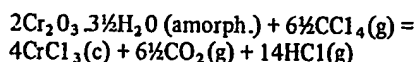
The reaction is preferably carried out at a temperature below  $600^\circ\text{C}$ ; when such temperatures are used, reaction equipment made from nickel and high nickel alloys can be used. Preferred reaction temperatures are from  $360^\circ$  to  $527^\circ\text{C}$ , the most preferred temperatures being from  $430^\circ$  to  $500^\circ\text{C}$ .

At temperatures below the glow temperature, the product,  $\text{CrCl}_3$ , does not sublime. At the same time the product is obtained in a sufficiently high purity not to need sublimation for the purpose of purification. The product obtained has a relatively high bulk density (substantially greater than the product obtained by volatilisation) and can be readily handled; it is suitable for use in the chromising process.

The chloridising reaction can be carried out in any suitable type of equipment for carrying out solid/gas heterogeneous phase reactions, for example a screw-conveyor type of reactor, a re-

circulating pneumatic reactor or a fluidised bed reactor. When carbon tetrachloride vapour is used as the chloridising agent, it can be condensed from the gases exiting from the reactor and recycled; hydrogen chloride, a product of the reaction (see below) can be recovered from the off-gases by scrubbing the latter with water.

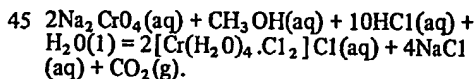
Using the preferred chloridising agent, carbon tetrachloride, a typical stoichiometric equation for the reaction is as follows:



When a mixture of carbon tetrachloride vapour and an inert gas, such as nitrogen, is used, the partial pressure of the carbon tetrachloride vapour is preferably from 90 to 212 mm Hg, more preferably about 90 mm Hg. The reaction rate is proportional to the space velocity of the gaseous reagent for space velocities up to about 170 mm/min at S.T.P. and is substantially independent of the space velocity at values of the latter from 170 to 284 mm/min at S.T.P.; it is preferred to use a space velocity of 170 to 284 mm/min at S.T.P., more preferably the lower end of this range.

The anhydrous chromic chloride product should be cooled in a non-oxidising atmosphere, preferably to a temperature below about 200°C. The bulk density of the final product is typically 0.75 g/cm<sup>3</sup> (poured) and 1.05 g/cm<sup>3</sup> (tapped). The product may be obtained in a sintered form, in which case grinding of the product may be desirable or necessary.

The chromic oxide hydrate used as the starting material is preferably obtained as follows. An aqueous solution of sodium chromate or dichromate is reduced to form a solution of a Cr III salt. This reduction can be effected, for example, with hydrochloric acid and methanol, preferably but not necessarily, at about 70°C, according to the equation:



This reaction is exothermic. Other reductants which can be used in place of methanol are, for example, ethanol, starch, cellulose, lignin, sugar, molasses, formic acid, sodium formate, acetic acid, ethylene glycol, sawdust, wood shavings, wood chips, paper waste, cotton waste, and lignite.

The Cr III salt solution obtained is neutralised, for example with magnesia or ammonia, to precipitate chromic oxide hydrate. Magnesia is preferably used in the form of an aqueous slurry of light magnesia or regenerated magnesia. The chromic oxide hydrate is separated and washing using, for example, a rotary drum vacuum filter, dried, for example in air at 110°C, and crushed, if necessary, to a suitably small particle size to facilitate the solid/gas hetero-

genous phase chloridising reaction. The chromic oxide hydrate is preferably such as to pass through a 36 B.S. mesh screen.

If desired, the dried chromic oxide hydrate may be dehydrated further prior to chloridisation, by being heated to a temperature below the glow temperature, preferably the chloridising temperature. Such dehydration may be carried out in any suitable environment, preferably non-oxidising, for example in a stream of a non-reactive gas or vapour, such as nitrogen, hydrogen or carbon monoxide, or in vacuo. Dehydration in a stream of nitrogen is preferred. The dehydrated product thus obtained is preferably not annealed prior to its being chloridised.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

#### Example 1

12 g of methanol were mixed with 0.86 l of a solution of 130 g/l of anhydrous sodium chromate in 219 g/l aqueous hydrochloric acid and allowed to react to completion. The aqueous chromic chloride solution thus obtained was heated to 80°C. Chromic oxide hydrate was precipitated at pH 6.85 by the addition, with gentle agitation, of 75.6 g of light magnesia in the form of a 10% w/v aqueous slurry. (There was no loss of chromium at this stage.)

The precipitated chromic oxide hydrate was filtered at 45°C, washed with 1 l of water and dried in air for 5 hours at 110°C (loss on drying: 75.5%; loss on ignition at about 700°C: 67.5%). The filtrate, 1.21 l, contained 24 g/l Na, 26.7 g/l Mg and 6 mg/l Cr; the wash liquor, 1.06 l, contained 1.7 g/l Na, 11.7 g/l Mg and 0.6 l Cr. (chromium recovery at this stage exceeded 99%). The dried chromic oxide hydrate was crushed and brushed through a 36 B.S. mesh screen. 1 g of the screenings was evenly distributed over the bottom of a silica boat (90 mm long x 16 mm wide x 13 mm deep), placed in a 28 mm diameter horizontal silica tubular reactor through which nitrogen gas was passed (space velocity: 254 mm/min at S.T.P.) and heated to 500°C and annealed for 1 hour. Carbon tetrachloride vapour (partial pressure: 83 mm Hg) was then mixed with the nitrogen gas and passed over the chromic oxide hydrate for a further period of 1 hour at 500°C.

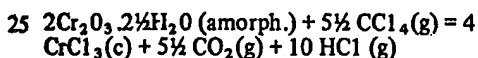
The chloridised product was cooled to ambient temperature in the stream of nitrogen gas. It exhibited the X-ray powder diffraction pattern and the diffuse reflectance spectrum of anhydrous chromic chloride. Furthermore, it was essentially insoluble in hot and cold dilute solutions of alkalis and hot and cold mineral acids, but dissolved rapidly and completely in dilute hydrochloric acid in the presence of zinc. The anhydrous chromic chloride product contained chlorine and chromium in a molar ratio of 3.14 : 1, the overall recovery of chromium was 98%.

#### Example 2

0.23 l of a gently agitated 337 g/l aqueous

solution of chromic chloride hexahydrate,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , was neutralised with 35% ammonia solution. The chromic oxide hydrate thus precipitated was filtered, washed with 0.2 l of water, re-pulped with 0.2 l of water and re-filtered thrice, and dried in air for 3 hours at  $110^\circ\text{C}$ . The dried chromic oxide hydrate contained 34.2% Cr and 5.35% Cl (loss on ignition at about  $700^\circ\text{C}$ : 46.6%).

The dried material was crushed and brushed through a 36 B.S. mesh screen. 1 g of the screenings was distributed evenly over the bottom of a silica boat (90 mm long x 16 mm wide x 13 mm deep), placed in a 28 mm diameter horizontal silica tubular reactor and heated to  $430^\circ\text{C}$  in a stream of nitrogen gas (space velocity: 156 mm/min at S.T.P.). Carbon tetrachloride vapour (partial pressure: 87 mm Hg) was introduced into the gas stream and passed over the chromic hydrate for 1 hour at  $430^\circ\text{C}$ . Chloridisation of the chromic oxide hydrate then occurred in accordance with the following stoichiometric equation:



Small amounts of carbon monoxide and chlorine were also evolved.

The product obtained was cooled to ambient temperature in the stream of nitrogen gas. The product was non-hygroscopic and exhibited the X-ray powder diffraction pattern, the infra-red absorption spectrum and the diffuse reflectance spectrum of anhydrous chromic chloride. It was essentially insoluble in hot and cold solutions of alkalis and hot and cold mineral acids, but dissolved readily and completely in dilute hydrochloric acid in the presence of zinc. The anhydrous chromic chloride product contained chlorine and chromium in a molar ratio of 2.98 : 1; the overall recovery of chromium was 98.5%.

#### WHAT WE CLAIM IS:

1. A process for the preparation of anhydrous chromic chloride, which comprises chloridising chromic oxide hydrate with a vapour or gas phase chloridising agent at an elevated temperature which is below the glow temperature and then cooling the anhydrous chromic chloride obtained in a non-oxidising atmosphere.

2. A process according to claim 1, in which the chloridising agent is carbon tetrachloride

vapour.

3. A process according to claim 1 or 2, in which the chloridising agent is used in admixture with an inert gas.

4. A process according to claim 3, in which the inert gas is nitrogen.

5. A process according to any of claims 1 to 4, in which the reaction is carried out at a temperature below  $600^\circ\text{C}$ .

6. A process according to any of claims 1 to 4, in which the reaction is carried out at a temperature of from  $360^\circ$  to  $527^\circ\text{C}$ .

7. A process according to any of claims 1 to 4, in which the reaction is carried out at a temperature of from  $430^\circ$  to  $500^\circ\text{C}$ .

8. A process according to any of claims 1 to 7, in which chloridising is effected with a mixture of carbon tetrachloride and an inert gas and the partial pressure of the carbon tetrachloride vapour is from 90 to 212 mm Hg.

9. A process according to any of claims 1 to 8, in which a stream of the chloridising agent is passed relative to the chromic oxide hydrate, the space velocity of the chloridising agent being from 170 to 284 mm/min at S.T.P.

10. A process according to any of claims 1 to 9, in which the chromic oxide hydrate starting material is prepared by reducing an aqueous solution of sodium chromate or dichromate to form a solution of a Cr III salt, neutralising the latter solution to precipitate chromic oxide hydrate, and separating, washing and drying the latter.

11. A process according to any of claims 1 to 10, in which the chromic oxide hydrate is dehydrated prior to chloridisation by being heated to a temperature below the glow temperature.

12. A process according to claim 11, in which such heating is effected in the presence of a stream of a non-reactive gas or vapour.

13. A process for the preparation of anhydrous chromic chloride substantially as herein described in either of the Examples.

14. Anhydrous chromic chloride when prepared by the process claimed in any of the preceding claims.

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